

Thermodynamic Stability – A note on a footnote in Ruelle’s book

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Abstract

Thermodynamic stable interaction pair potentials which are not of the form “positive function + real continuous function of positive type” are presented in dimension one. Construction of such a potential in dimension two is sketched. These constructions use only elementary calculations. The mathematical background is discussed separately.

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1 Introduction

In Ruelle’s book [R69] on statistical mechanics, in section 3.2 concerning one species of classical particles in \mathbb{R}^{ν} , you can read:

1 PROPOSITION. *If the pair potential Φ can be written in the form*

$$\Phi = \Phi_1 + \Phi_2 \tag{1}$$

where Φ_1 is positive, and Φ_2 is a real continuous function of positive type, then Φ is stable.

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“Positive” is meant here and throughout this paper as nowhere negative, “stable” means

$$\exists E_0 \in \mathbb{R} \text{ such that } \forall N, \forall \{x_1 \dots x_N\} \subset \mathbb{R}^\nu : U(x_1 \dots x_N) \geq N \cdot E_0, \quad (2)$$

$$\text{where } U(x_1 \dots x_N) = \sum_{i \neq j} \Phi(x_j - x_i). \quad (3)$$

This proposition is accompanied by the

2 FOOTNOTE. *It seems to be an open problem to construct a stable potential which is not of the form (1).*

We solve this problem in dimension 1, considering particles either in \mathbb{Z} or in \mathbb{R} , giving a detailed proof. In dimension 2 the problem can also be solved, but we give only a sketch of the ideas.¹

To make it simple, we consider only pair potentials which are bounded continuous functions and state the stability property as

3 DEFINITION. *A bounded continuous real valued function V on \mathbb{R}^ν is stable, if*

$$E(\rho) := \int \int \rho(x) V(x - y) \rho(y) d^\nu x d^\nu y \geq 0 \quad (4)$$

for every positive finite measure $\rho(x) d^\nu x$ on \mathbb{R}^ν . A bounded real valued function V on \mathbb{Z}^ν is stable, if

$$E(\rho) := \sum_{\vec{m}} \sum_{\vec{n}} \rho(\vec{m}) V(\vec{m} - \vec{n}) \rho(\vec{n}) \geq 0 \quad (5)$$

for every positive bounded function $\rho(\vec{m})$ on \mathbb{Z}^ν .

The stability property used in Ruelle’s Theorem is an immediate consequence. With $\rho = \sum_{i=1}^N \delta(x_i - x_j)$ put into equation (4) one gets

$$U(x_1 \dots x_N) = E(\rho) - N \cdot V(0) \geq -N \cdot V(0).$$

The main result of our considerations is stated as

4 THEOREM. *Each of the following functions is a stable pair potential, but not a sum of a positive and a real valued positive definite function.*

1. *The function $V : \mathbb{Z} \rightarrow \mathbb{R}$, defined as*

$$\begin{aligned} V(0) = V(2) = V(-2) = 1, \quad V(1) = V(-1) = -1, \\ V(n) = 0 \quad \forall n \text{ with } |n| \geq 3, \end{aligned} \quad (6)$$

2. *The function $W : \mathbb{R} \rightarrow \mathbb{R}$, defined as*

$$W(x) = \sum_{n \in \mathbb{Z}} \int_{-\infty}^{\infty} V(n) f(n - x + y) f(y) dy, \quad (7)$$

with f a positive continuous function $(-\frac{1}{2}, \frac{1}{2}) \rightarrow \mathbb{R}$ and V as defined in (6).

¹ Construction in higher dimensions is still an open problem.

2 Properties of the interaction potentials

Proof. Of part (1) of 4 Theorem.

Denote the distribution of particles on the chain by the “density” ρ , a function $\mathbb{Z} \rightarrow \mathbb{Z}_+$. The interaction energy U becomes smaller, when the system is cut into non-interacting pieces: If $\rho(n) \geq \rho(n+1)$ divide the chain, cutting between $n+1$ and $n+2$. Moving the pieces apart, one loses the energy

$$2[\rho(n) - \rho(n+1)]\rho(n+2) + 2\rho(n+1)\rho(n+3) \geq 0.$$

The symmetric procedure of cutting between $n-2$ and $n-1$ lowers the energy if $\rho(n-1) \leq \rho(n)$.

Now there remains a set of pieces of no more than three lattice points, with densities like

$$0 \leq \rho(n-1) \leq \rho(n) \geq \rho(n+1) \geq 0.$$

Including the “self-energies” $N \cdot V(0)$ one gets for each piece, centered around n ,

$$\begin{aligned} E &= \rho(n-1)^2 + \rho(n)^2 + \rho(n+1)^2 + 2[\rho(n-1)\rho(n+1) - \rho(n-1)\rho(n) - \rho(n)\rho(n+1)] \\ &= [\rho(n-1) - \rho(n) + \rho(n+1)]^2 \geq 0. \end{aligned}$$

Proving the stability of V .

If V were the sum of a positive and a positive definite function, it would give

$$\sum_n V(n)\mu(n) \geq 0, \quad (8)$$

for each μ being both positive and positive definite. Now consider

$$\mu(5\nu) = 1, \quad \mu(5\nu \pm 1) = \frac{\sqrt{5} - 1}{2}, \quad \mu(5\nu \pm 2) = 0, \quad (9)$$

which is obviously positive. Positive definiteness is seen by using Bochner’s theorem [RN55] and calculating the Fourier-Transform, with $\alpha \in (-\pi, +\pi]$:

$$\begin{aligned} \hat{\mu}(\alpha) &= \sum_n \mu(n)e^{-in\alpha} \\ &= \frac{2\pi}{5} \left[\sqrt{5} \delta(\alpha) + \frac{5 - \sqrt{5}}{2} \left(\delta(\alpha - \frac{2\pi}{5}), +\delta(\alpha + \frac{2\pi}{5}) \right) \right] > 0. \end{aligned} \quad (10)$$

But it does not give a positive value in (8):

$$\sum_n V(n)\mu(n) = 2 - \sqrt{5} < 0.$$

□

The appearance of the numbers 5 and $\sqrt{5}$ may seem mysterious. Demystifying is the next section, where we present the “origin” of these V and μ .

In this section we develop further use of these functions in \mathbb{R} and in \mathbb{R}^2 .

Proof. Of part (2) of 4 Theorem.

For N particles at $x_1 \dots x_N$ consider the measure

$$\rho(x) = \sum_j \delta(x - x_j). \quad (11)$$

Adding the self-energies $N \cdot W(0)$, we study

$$\begin{aligned} E &= \int \int \rho(x) W(x - y) \rho(y) dx dy \\ &= \sum_n V(n) \int \rho_f(x + n) \rho_f(x) dx, \end{aligned} \quad (12)$$

with $\rho_f(x) := \int f(x - y) \rho(y) dy$. Splitting the integral in (12) into pieces of intervals with unit length and defining $\rho_{f,x}(m) = \rho_f(x + m)$ gives

$$\begin{aligned} E &= \sum_{m \in \mathbb{Z}} \int_0^1 dx \sum_n V(n) \rho_f(x + m + n) \rho_f(x + m) \\ &= \int_0^1 dx \sum_{p \in \mathbb{Z}} \sum_{m \in \mathbb{Z}} \rho_{f,x}(p) V(p - m) \rho_{f,x}(m) \geq 0, \end{aligned}$$

by part (1) of the theorem. So the potential W is stable.

Now consider the distribution

$$\mu_D(x) = \sum_m \mu(m) \delta(x - m), \quad (13)$$

using the sequence μ defined in (9). This distribution is positive and positive definite, as can be seen at its Fourier transform, which is (up to a factor) the same as in (10), now with $\hat{\mu}_D(\alpha + 2\pi) = \hat{\mu}_D(\alpha)$ periodically extended to all $\alpha \in \mathbb{R}$. This μ_D is used to show that the potential is not a sum of positive and positive definite functions:

$$\begin{aligned} &\int W(x) \mu_D(x) dx \\ &= \sum_n V(n) \sum_m \mu(m) \int_{-\frac{1}{2}}^{+\frac{1}{2}} dy \int_{\mathbb{R}} dx \delta(x - m) f(n - x + y) f(y) \\ &= \sum_n V(n) \mu(n) \cdot \int f^2(y) dy < 0. \end{aligned} \quad (14)$$

In the last step the final support of f is essential. \square

Construction of a stable pair potential in \mathbb{R}^2 being a function of the particle distances only may be done in the following way:

- Use $W(x)$ defined in (7), now with an f supported on $(-\frac{1}{4}, \frac{1}{4})$, convolute it twice with the distribution

$$h(x) = \sum_{n \in \mathbb{Z}} e^{-\epsilon|n|} \delta(x - 5n) :$$

$$W_1(x) = \int \int h(x - y) W(y - z) h(z) dy dz.$$

- Take the mean value (times 2π) of all rotated versions: $W_r(\vec{x}) = \frac{1}{r} W_1(|\vec{x}|)$.
- Smoothen out W_r with a positive continuous function $g(r)$ with support on $[0, \frac{1}{4}]$:

$$W_2(\vec{x}) = \int \int g(|\vec{x} - \vec{y}|) \frac{W_1(|\vec{y} - \vec{z}|)}{|\vec{y} - \vec{z}|} g(|\vec{z}|) d^2y d^2z.$$

That the stability is not destroyed by the double convolution with h follows from a consideration as it is used in the equation (12). Written in a formal way:

$$\langle \rho | W_1 | \rho \rangle = \langle \rho | h * W * h_- | \rho \rangle = \langle \rho * h | W | \rho * h \rangle.$$

Considering only smooth densities $\rho(\vec{x})$ one may take $W_1(x_1)\delta(x_2)$ as a stable distribution in \mathbb{R}^2 :

$$\langle \rho | W_1 \cdot \delta | \rho \rangle_{dim=2} = \int \langle \rho_y | W_1 | \rho_y \rangle_{dim=1} dy \geq 0.$$

Now rotating the axes and taking the mean value does not destroy the stability. Once more a double convolution is done, now with g in order to get W_2 as a bounded continuous potential acting in \mathbb{R}^2 .

$$\langle \rho | W_2 | \rho \rangle = \langle \rho | g * W * g_- | \rho \rangle = \langle \rho * g | W | \rho * g \rangle \geq 0.$$

Smoothing by convolution with g enables to consider again sets of particles represented by delta-functions in ρ .

To disprove the possibility of splitting W_2 into a sum of a positive and a positive definite function one may use the μ_D of equ. (13) embedded into \mathbb{R}^2 ,

$$\mu_D(x, y) = \mu_D(x)\delta(y).$$

Due to the smoothing of W_r by g and due to its decrease given by the decrease of h , the integral $\int W_2 \mu_D$ is finite:

$$\int W_2 \mu_D(x) dx = W_2(0) + 2W_2(1)\mu(1) + 2 \cdot \sum_{\nu=1}^{\infty} \sum_{n=-2}^{+2} W_2(|5\nu + n|) \mu(n)$$

The bounded support of f and g is needed here as it was in equ. (14). The exponential decrease implies

$$W_2(|5\nu + n|) = \text{const.} \cdot e^{-5\epsilon\nu} \frac{1}{5\nu} V(n) \cdot \left(1 + O\left(\frac{1}{\nu^2}\right)\right).$$

The “const.” factor involves the integrals over f^2 and g^2 , the error term $O(\frac{1}{\nu^2})$ gives the difference between $e^{-5\epsilon\nu}/5\nu$ and $e^{-\epsilon(5\nu+n)}/(5\nu + n)$. The summations over ν and n give

$$\approx 2 \cdot \text{const.} \cdot \sum_{n=-2}^{+2} V(n) \mu(n) \cdot \log(1/\epsilon) + O\left(\sum_{\nu=1}^{\infty} e^{-5\epsilon\nu} \frac{1}{\nu^2}\right).$$

The first part is negative and increases without limit when $\epsilon \rightarrow 0$, while the other term remains finite. So W_2 with small ϵ can **not** be a sum of positive and positive definite functions.

3 Mathematical background

Only in applying Proposition 1 in statistical mechanics the Thermodynamic Limit is considered, not yet in the investigations of “stability”. Moreover, in the reformulation in 3 Definition there is no mentioning of “particles”. What is used of properties of space are: A distance relation between points and an invariant measure. This allows for a more general version of the definition, concerning functions on groups. We keep the notation we used above: x and y are elements of the group, their “group product” is $x + y$, the “inverse” of x is $-x$.

5 DEFINITION. *Consider a bounded continuous real valued function V on a locally compact abelian group G which has the Haar measure dx . V is stable, if*

$$\langle \rho | V | \rho \rangle := \int \int \rho(x) V(x - y) \rho(y) dx dy \geq 0 \quad (15)$$

for every finite positive Borel measure $\rho(x)dx$.

Stable functions can be added, multiplied by positive numbers, and limits may be formed. So they form a closed convex cone, which we call STB. This cone STB contains POS, the cone of positive functions, also PDF, the cone of positive definite functions and sums thereof.

$$\text{STB} \supset \text{POS} + \text{PDF} \quad (16)$$

An investigation of the relations between these cones may proceed via investigation of the dual cones (see [V64, R62, G03]). The dual cones are subsets of \mathcal{V}' , the space of finite Borel measures $\mu(x)dx$, which is the dual space to \mathcal{V} , the

Banach space of bounded continuous functions. The dual cone to POS is POS', the set of finite positive Borel measures, dual to PDF is PDF', the set of finite positive definite Borel measures. The cone STB' is given as the closure of the cone of convex combinations of “correlation measures”

$$\mu(x) = \int_G \rho(x)\rho(y+x)dy, \quad (17)$$

i.e. convolutions of finite positive Borel measures $\rho(x)dx$ with their reflected version $\rho(-x)dx$. These correlation measures are both positive and positive definite:

$$STB' \subset POS' \cap PDF' \quad (18)$$

Now the question of equality or inequality in this relation is related to the central problem which is our concern in this investigation, the question of equality or inequality in (16). If the closed cone $POS' \cap PDF'$ contains an element μ which is not in the closed cone STB' , then, by definition of “dual cone”, there exists an element $V \in STB$ such that $\int V\mu < 0$, incompatible with a decomposition $V = f + g$, $f \in POS$, $g \in PDF$.

For the groups \mathbb{Z}_2 , \mathbb{Z}_3 , \mathbb{Z}_4 there is equality in the equations (16) and (18), but not for \mathbb{Z}_5 .

6 PROPOSITION. *The intersection of $POS' \cap PDF'$ with the plane $\{(\mu(-2) \dots \mu(2)) | \mu(0) = 1\}$ is completely characterized by its extremal points $(0, 0, 1, 0, 0)$, $(0, \gamma, 1, \gamma, 0)$, $(\gamma, 0, 1, 0, \gamma)$, $(1, 1, 1, 1, 1)$, with $\gamma = (\sqrt{5} - 1)/2 = 1/(2|\cos 4\pi/5|)$.*

Proof. By using Bochner's theorem and analyzing the Fourier transform

$$\hat{\mu}(k) = \sum_{n=-2}^2 \mu(n)e^{-2\pi kn/5}. \quad (19)$$

□

On the other hand there is a bound for STB' which cuts off a triangular subset of this convex quadrangle:

7 LEMMA. *Each element of STB' obeys the inequality*

$$\mu(1) \leq \sum_{n=-2}^2 \mu(n)/4. \quad (20)$$

Proof. STB' is defined by its extremal rays, formed as correlation measures of positive densities.

$$\mu \in STB', \quad \mu \text{ extremal} \quad \Leftrightarrow \quad \exists \rho \geq 0, \quad \mu(n) = \sum_{m=-2}^2 \rho(m)\rho(m+n).$$

Assume, w.l.o.g., that $\rho(-1) \geq \rho(-2)$. then

$$\begin{aligned}\mu(1) &= [\rho(-1) + \rho(1)] \cdot [\rho(-2) + \rho(0) + \rho(2)] - [\rho(-1) - \rho(-2)] \rho(2) - \rho(-2)\rho(1) \\ &\leq \left(\frac{s}{2} - x\right)\left(\frac{s}{2} + x\right) \leq \frac{s^2}{4}.\end{aligned}$$

Here $s = \sum_m \rho(m)$, $x = [\rho(-2) + \rho(0) + \rho(2) - \rho(-1) - \rho(1)]/2$.

Observe $\sum_n \mu(n) = s^2$. \square

Remark: Also $\mu(2)$ obeys this inequality and $\mu(-1) = \mu(1)$, $\mu(-2) = \mu(2)$. Closer inspection reveals moreover two rounded edges of STB' .

Now the extremal point with $\mu(n)$ as in equation (9) with $\nu = 0$ is outside this boundary. And $V(n)$ as in equation (6) is an element of STB , but *outside* of POS+PDF .

4 Conclusion

For pair potentials which are bounded continuous functions the property of being “stable” can be reformulated without mention of particles. In this way it can be studied for abstract abelian groups. At the heart of the present investigation is the observation of a function V in \mathbb{Z}_5 which is stable, but indecomposable into a sum of positive and positive definite functions. This function V can also be used on \mathbb{Z} . With some smoothing it can be used on \mathbb{R} , and in damped periodically extended, rotationally symmetrized and again smoothed form on \mathbb{R}^2 . Of course it is possible find sets of other examples nearby. So $V(-1) = V(1)$ in Theorem 4 could be a little bit higher than -1 . Only at $-(\sqrt{5}+1)/4 \approx -0.8$ does it become decomposable.

The construction of a rotationally invariant example for dimension two is not so simple. A nicer one, or one for higher dimension, is not yet known.

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